Uppsala 1963

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Band 20 nr 37

ROLF HESSE

The crystal structure of copper(I) diethyldithiocarbamate and its interpretation

An application of chemical topology

ALMQVIST & WIKSELL

STOCKHOLM

GÖTEBORG · UPPSALA

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THE CRYSTAL STRUCTURE OF COPPER(I)DIETHYLDITHIOCARBAMATE AND ITS INTERPRETATION

An application of chemical topology

BY

ROLF HESSE

FIL. LIC., ÖG.

By due permission of the Faculty of Science
of the University of Uppsala to be publicly discussed
in the lecture hall of the Institute of Chemistry,
April 8, 1963, at 10 a.m., for the degree of Doctor
of Philosophy

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ARKIV FÖR KEMI Band 20 nr 37

Communicated 5 December 1962 by Gunnar Hägg and Arne Fredga

The crystal structure of copper(I)diethyldithiocarbamate and its interpretation

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By Rolf Hesse

Introduction

Investigations in Uppsala on coinage metal dithiocarbamates were initiated by A. Fredga [1] and in recent years have been continued by S. Åkerström [2], engaging in preparative and physico-chemical studies, and the present author working on the determination of their crystal structures. Short descriptions of some of these structures have already been given by the author [3, 4]. Detailed accounts of the structure investigations and their results will now be published in a series of papers.

The dialkyldithiocarbamates of copper(I), silver(I) and gold(I) form polymeric molecules in the solid state and in solutions of various organic solvents. Their formula can be written

$$[R_2NCS_2M]_P$$

where R = alkyl, M = Cu, Ag or Au and P = degree of polymerity. P has different values, mainly 2, 4 and 6. Accordingly the majority of the compounds are low polymers but some of the lower homologues are probably high polymers.

A common feature of the low polymers studied so far is that they contain central metal groups with short metal-metal distances. Thus the structure investigations have demonstrated the occurrence of groups such as Cu_4-tetrahedra, Ag_6-chains, Ag_6-octahedra and Au_2-pairs.

The metal atoms are generally coordinated by the sulphur atoms of the thiocarbamate molecules and the metal coordination is in many cases very interesting. Thus it is threefold in the copper and silver compounds investigated; in the gold compounds, however, it is linear in the usual fashion.

The structures are most often complicated but topological considerations indicate that some of them at least are of the simplest type possible under the conditions which obtain. It is reasonable to expect that a number of other AX-compounds, where A is metal and X is a bulky organic group, which can only be linked in a very unsymmetric way, will present similar linkage problems as these thiocarbamates. For this reason some investigations on mercaptides have also been started in this Institute.

In the following treatment the determination and interpretation of the copper(I)-diethyldithiocarbamate structure will be presented.

Table 1. Details of crystals, rotation axes and recorded layers in the single crystal work.

	Crystal 1	Crystal 2	Crystal 3
Recrystallized from	chloroform, ether	chloroform, ether	CS_2 petrol
Shape	shortened needle	fragment of needle	shortened needle
Dimensions (mm)	0.1 0.1 0.3	0.1 0.1 0.1	0.04 0.04 0.25
Rotation axis	[001] needle axis	[110]	[001] needle axis
Recorded reflexions	*hkL* $L = 0$–6	*h*, *N*–*h*, *l* $N = 0$–7	*hkL* $L = 0$–7

Experimental

Samples of copper(I)diethyldithiocarbamate were supplied by A. Fredga and S. Åkerström who had prepared them according to their published methods [1, 2]. The crystals used were obtained from chloroform and ether or from carbon disulphide and petrol as tetragonal yellow needles (needle axis [001]) with almost square cross section and faces of the form {110} developed. Their density was measured by flotation in an aqueous solution of K_2HgI_4. Unit cell dimensions were determined from a Guinier photograph using elementary silicon ($a = 5.4305$ Å [5]) as a calibrant (Cr–$K\alpha_1$-radiation, $\lambda = 2.2896$ Å [6]).

Three crystals (see Table 1) were used for the single crystal work. The reflexions were recorded on equi-inclination Weissenberg photographs using Cu-*K* radiation. Rotation axes and recorded layers are given in Table 1. The relative intensities were estimated visually by using multiple film technique and comparing with an intensity scale. The data were corrected for the Lorentz and polarisation effects. No corrections were made for absorption.

Early intensity data for 215 independent reflexions were obtained from crystals 1 and 2 using radiation of rather low intensity (gas tube). Following LP correction the intensities were brought to a common scale by systematic interlayer comparisons and averaged. This set of data was used in the first stages of the structure determination up to the estimation of approximate atomic coordinates.

For the final refinement a new set of intensity data corresponding to 716 nonequivalent reflexions were collected from crystal 3 using a more intense source of radiation (sealed tube). Comparison of the two sets of data indicated an appreciable difference between the overall temperature factors. Thus the *B*-value for the later data was lower than that for the earlier by 1.0 Å^{-2}. After multiplying the earlier structure factors by $\exp(1.0 \sin^2\theta/\lambda^2)$ and referring those from crystal 3 to the same scale the *F*-values from the two sets of data were averaged with equal weights. The combined set so obtained was used for the final refinement. It comprised structure factors for 728 independent reflexions and was almost completely dominated by the data from crystal 3.

Computational aids

The Hägg-Laurent [7] analogue computer for Fourier series was used in the first stages of the structure determination. For the final refinement structure factor,

Fourier series and least squares calculations were performed on the electronic computers BESK and FACIT in Stockholm using programmes designed by Westman, Blomqvist, Åsbrink, Liminga, Olovsson and Brändén [8, 9, 10, 11].

Crystal data

Copper(I)diethyldithiocarbamate, $C_5H_{10}NS_2Cu$
Tetragonal, $a = 13.494 \pm 0.006$ Å, $c = 9.335 \pm 0.005$ Å
Volume of unit cell: 1700 Å^3
Density (measured): 1.68 g cm^{-3}
Density (calculated): 1.66 g cm^{-3}
Eight formula units per unit cell
Diffraction symmetry: $4/mmm$
Systematic absences: hhl if l is odd
$h00$ if h is odd
Space group: No 114 $P\bar{4}2_1c$

Structure analysis

Copper and sulphur positions

The general features of the Pattersson function were evaluated from the bounded projections:

$$\int_{(2n-1)/20}^{(2n+1)/20} P(uvw)\,du \quad \text{with } n = 0, 1, 2, 3, 4, 5$$

Employing the symmetry of the function, the coordinates u, v, w, of all the stronger maxima could be determined with sufficient accuracy from these projections. The five strongest maxima (that at the origin neglected) could be interpreted as Cu–Cu peaks from which approximate copper coordinates were obtained as follows: $x = 0.07$, $y = 0.07$, $z = 0.10$.

Fourier projections in the [001] and [010] directions were then calculated using structure factors with $h+k = 2n$ and $h+l = 2n$, the signs being determined from the copper positions. Terms with $h+k = 2n+1$ and $h+l = 2n+1$ could not be introduced since at this stage of the structure determination $x_{Cu} = y_{Cu}$. The projections were thus obscured by false symmetry elements but it was possible to deduce reasonable sulphur positions from the [010] projection. These positions were confirmed from the Pattersson function. Signs could then be allocated to structure factors of $hk0$ and $h0l$ reflexions for which $h+k = 2n+1$ and $h+l = 2n+1$ and the copper and sulphur coordinates were roughly refined by subsequent electron density projections.

Nitrogen and carbon positions

The nitrogen and carbon atoms could not be detected in the electron density projections used so far but their approximate positions could be determined from a difference synthesis projection in the [010] direction (see Fig. 1*a*) with Cu and S subtracted. This was interpreted by geometrical constructions based on the following assumptions regarding the shape and dimensions of the diethyldithiocarbamate molecule (notation of the atoms, see Fig. 4): $S_1 - S_2 = 3.1$ Å (from the established sulphur positions); $C_1 - S_1 = C_1 - S_2 = 1.7$ Å; $C_1 - N = 1.4$ Å; $S_1S_2C_1N$ coplanar; $N - C_2 =$

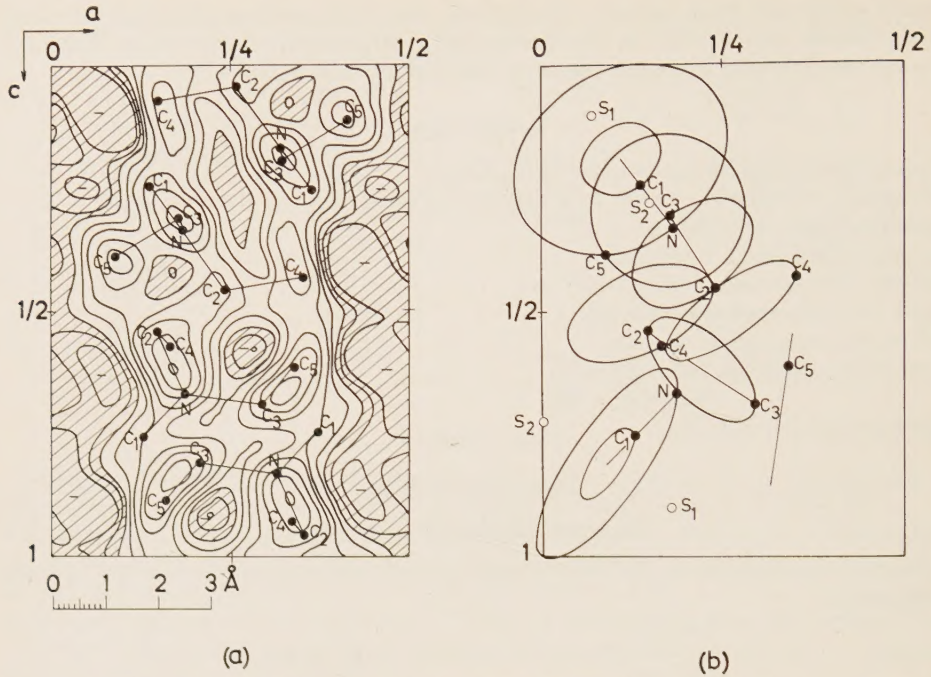

Fig. 1. (a) Difference synthesis projection based on $h\,0\,l$ structure factors. Copper and sulphur contributions subtracted.

(b) Constructions for the interpretation of the synthesis. Curves are drawn for two symmetry-related molecules.

$N-C_3=1.5$ Å; $\angle C_1NC_2=\angle C_1NC_3=\angle C_2NC_3=120°$; $C_2-C_4=C_3-C_5=1.5$ Å; $\angle NC_2C_4=\angle NC_3C_5=110°$.

Using this data and starting from the known sulphur positions the loci of the light atoms were successively constructed. The construction curves for two symmetry-related molecules are given in Fig. 1*b*.

In the projection the atoms C_1 and N of the molecules under consideration are located on two pairs of concentric ellipses and on the same radius vector in each of these pairs. The two radius vectors concerned are related to each other by symmetry. Accordingly when the position of *one* of these four carbon and nitrogen atoms is fixed in the projection the positions of the other three are also fixed. The atoms considered could be located by superposing their construction curves on the difference map and applying the radius vector and symmetry relationships. The atomic positions best fitting the difference synthesis are marked in the figure.

The carbon atoms C_2, C_3, C_4 and C_5 were then located by similar constructions. Their best positions are seen in the figure. If small changes in the coordinates are neglected, this interpretation has no alternative. As a good check it was found that the group $S_1S_2C_1NC_2C_3$ was almost coplanar, an expected feature of the structure which, however, had not been used in the constructions. Another check was lowering of the reliability index for both $hk0$ and $h0l$ reflexions to approximately half of their earlier values following the introduction of the light atoms into the structure factor calculations.

Refinement

The coordinates of all but the hydrogen atoms were refined first by successive three-dimensional backshift cycles and then as a suitable program became available by three-dimensional least squares analysis using only observed reflexions. The least squares program [11] was based on a diagonal block approximation of the matrix with blocks of 3×3 elements corresponding to atomic coordinates, and "blocks" of 1×1 elements corresponding to isotropic temperature factors. A weight factor, $\omega = 1/(a + |F| + c|F|^2)$, with $a = 2|F_0(\min)|$ and $c = 2/|F_0(\max)|$, as suggested by Cruickshank [12], was used. The atomic scattering factors were taken from the following sources: copper, Thomas and Umeda [13]; sulphur, Tomiie and Stam [14]; nitrogen and carbon, Berghuis *et al.* [15]. The real part, $\Delta f' = -2.1$, [16], of the dispersion correction for copper was introduced in the calculations.

The refinement was continued until the shifts were approximately one tenth of the calculated standard deviations. The R-value at this point was 0.11. The final atomic coordinates and the corresponding isotropic temperature factors are given in Table 2. Tables of observed and calculated structure factors may be obtained on request from the Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

The least squares program, which had been designed for orthorhombic and lower symmetries, could nevertheless be applied to this tetragonal structure for the refinement of coordinates and temperature factors, but not for the determination of standard deviations. The approximate standard deviations given in Table 2 were calculated from the final $\Delta|F|$-values and the curvatures of the maxima in a F_0-synthesis according to Cruickshanks formula [17], taking account of non-centrosymmetry [18]. The rough approximations involved in this formula, for instance putting $\sigma|F| = \Delta|F|$ (which is also used in the least squares method), should of course be kept in mind.

The combined set of F_0-values is almost completely dominated by the data from crystal 3 for which the absorption errors capable of influencing the coordinates are small. Nevertheless the temperature factor B-values may be affected to some extent by absorption. The fact that the overall temperature factors for the earlier and later sets of data (both taken at room temperature; the effect opposite to the trend of absorption) exhibit differences seems to indicate that they are influenced by disorder phenomena. Similar effects have also been found in studies of some other dithiocarbamate complexes. It may finally be mentioned that the highest B-values of the

Table 2. Final atomic coordinates.

Atom	x/a	y/b	z/c	σ(Å)	B(Å^2)
Cu	0.0704	0.0740	0.0967	0.003	3.15
S_1	0.1680	0.0680	−0.1038	0.005	3.06
S_2	−0.0021	0.1489	−0.2817	0.006	4.13
N	0.1885	0.1828	−0.3348	0.022	3.85
C_1	0.1200	0.1350	−0.2445	0.025	4.02
C_2	0.1583	0.2414	−0.4643	0.028	4.75
C_3	0.2955	0.1779	−0.3098	0.029	4.14
C_4	0.1454	0.3499	−0.4202	0.040	6.21
C_5	0.3415	0.0877	−0.3869	0.034	6.30

The notation of the atoms corresponds to that used in Fig. 3.

Table 3. Interatomic distances and angles.

Atoms	Distances (Å)	σ (Å)	Atoms	Distances (Å)	σ (Å)
		Intramolecular distances and angles			
$Cu_I - Cu_{II}$	2.658	0.005	$S_1 - S_2$	3.037	0.008
$Cu_I - Cu_{III}$	2.757	0.005	$S_1 - C_1$	1.721	0.027
$Cu_I - S_{1,I}$	2.290	0.006	$S_2 - C_1$	1.695	0.025
$Cu_I - S_{1,II}$	2.258	0.005	$N - C_1$	1.408	0.033
$Cu_I - S_{2,IV}$	2.246	0.007	$N - C_2$	1.501	0.037
			$N - C_3$	1.464	0.032
$S_{1,I} - S_{1,II}$	3.96				
$S_{1,I} - S_{2,IV}$	3.72		$C_2 - C_4$	1.530	0.044
$S_{1,II} - S_{2,IV}$	4.04		$C_3 - C_5$	1.544	0.046

Atoms	Angle	σ	Atoms	Angle	σ
$S_{1,I} - Cu_I - S_{1,II}$	121°3	0°2	$S_1 - C_1 - S_2$	125°5	1°7
$S_{1,I} - Cu_I - S_{2,IV}$	110°0	0°3	$S_1 - C_1 - N$	116°8	2°0
$S_{1,II} - Cu_I - S_{2,IV}$	127°6	0°3	$S_2 - C_1 - N$	117°7	2°1
$Cu_I - S_{1,I} - Cu_{IV}$	71°5	0°2	$C_1 - N - C_2$	123°0	2°4
$Cu_I - S_{1,I} - C_{1,I}$	112°9	1°0	$C_1 - N - C_3$	122°2	2°5
$Cu_{IV} - S_{1,I} - C_{1,I}$	104°2	1°0	$C_2 - N - C_3$	114°8	2°4
$Cu_{II} - S_{2,I} - C_{1,I}$	102°1	1°0	$N - C_2 - C_4$	108°6	2°6
			$N - C_3 - C_5$	110°9	2°7

Atoms	Distance (Å)	Atoms	Distance (Å)
	Intermolecular distances shorter than 4.0 Å		
$C_{2,I} - C_{3,V}$	3.94	$C_{4,I} - Cu_V$	3.94
$C_{2,I} - C_{5,II(-)}$	3.84	$C_{4,I} - S_{1,IV}$	3.88
$C_{3,I} - Cu_V$	3.92	$C_{4,I} - C_{5,II(-)}$	3.63
$C_{3,I} - S_{1,V}$	3.90		
$C_{3,I} - S_{2,VIII}$	3.69	$C_{5,I} - C_{2,IV(-)}$	3.84
$C_{3,I} - C_{2,V(+)}$	3.94	$C_{5,I} - C_{4,IV(-)}$	3.63

The notation of the atoms corresponds to that used in the diagrams (see for instance Figs. 2 and 3). The Roman numeral (I) has been omitted in cases where the atoms under consideration are situated in the same dithiocarbamate molecule.

individual isotropic temperature factors are associated with the outermost carbon atoms, which would be the ones most easily affected by thermal motion or disorder effects.

Description of the structure

Interatomic distances and angles are given in Table 3, together with their calculated standard deviations and isotropic temperature factors. For the notation of atoms and molecules, see Figs. 2–5.

Molecular arrangement

The crystal structure of copper(I)diethyldithiocarbamate is built up from discrete $[(C_2H_5)_2NCS_2Cu]_4$-molecules, of which there are two per elementary cell, with their

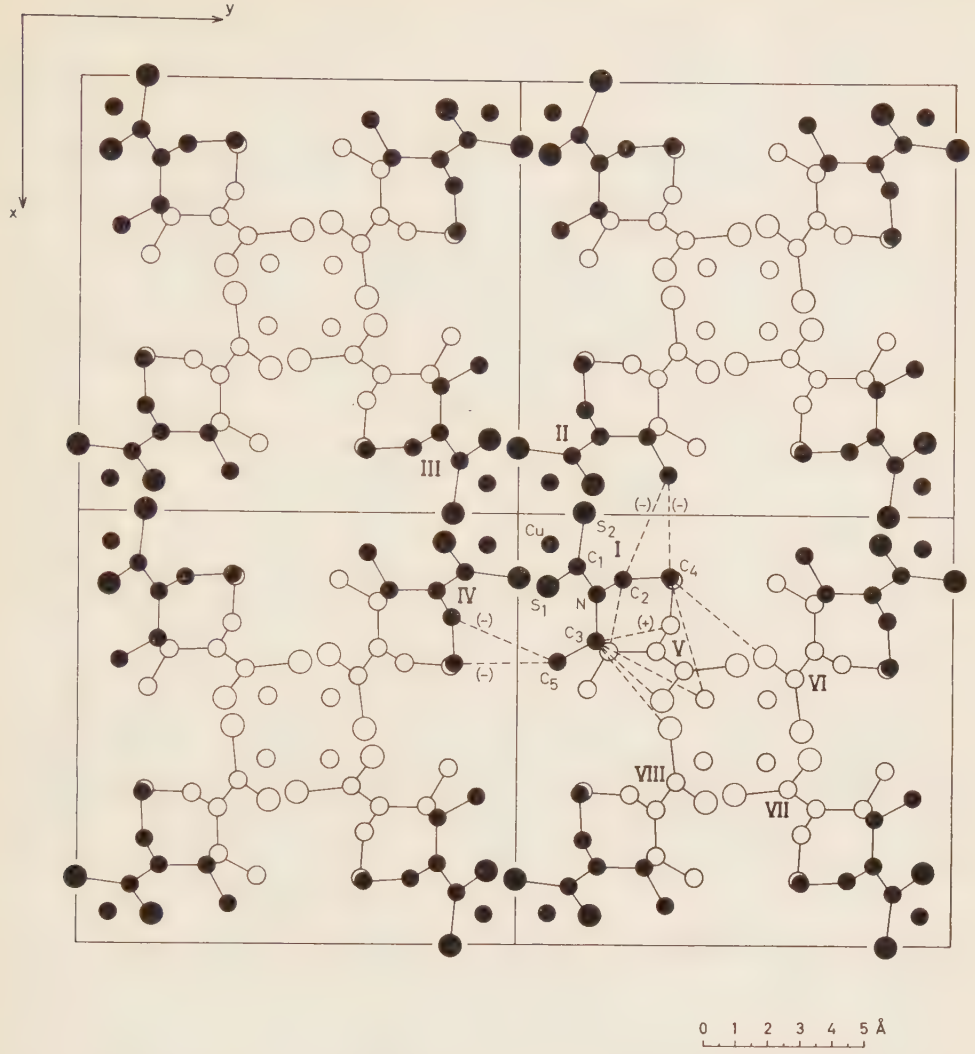

Fig. 2. Crystal structure of copper(I)diethyldithiocarbamate. [001]-projection. Four elementary cells. The $[(C_2H_5)_2NCS_2Cu]_4$-molecules given by black circles have their molecular centres at $z = 0$, those given by unfilled circles have centres at $z = -\frac{1}{2}$. The broken lines indicate intermolecular distances shorter than 4.0 Å (see Table 3). The designation (+) or (−) at the terminal of a line means that the line terminates at an atom situated one translation unit above or below that seen in the diagram.

centres at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The symmetry relation between the two molecules of the unit cell is that of a glide plane c making the intercepts $\frac{1}{2},\frac{1}{2}$ on the x- and y-axes. The packing of the molecules is seen in Fig. 2, in which the broken lines indicate intermolecular distances shorter than 4 Å (hydrogen atoms neglected).

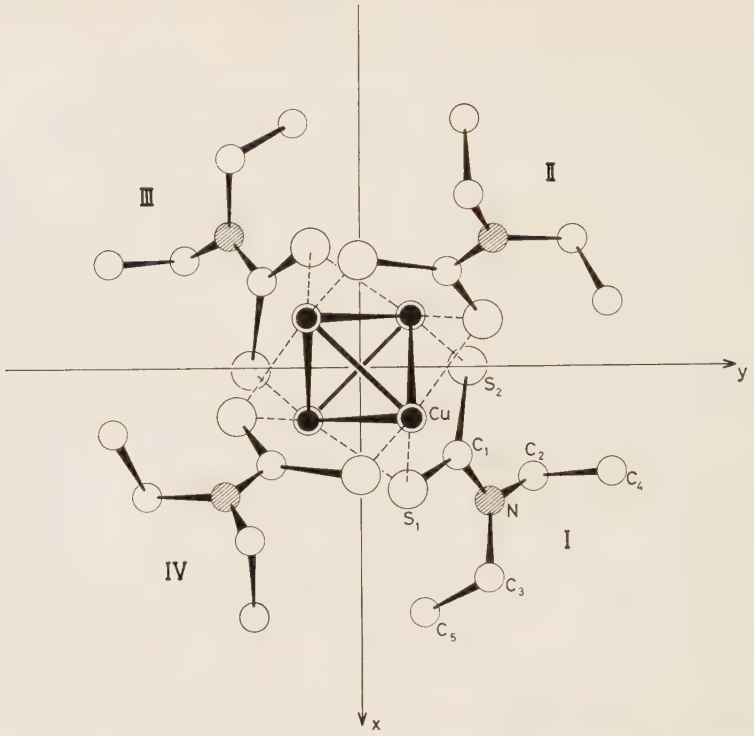

Fig. 3. $[(C_2H_5)_2NCS_2Cu]_4$-molecule. [001]-projection. Molecular symmetry $\bar{4}$. Molecular centre at 0,0,0. The diethyldithiocarbamate molecules I and III are situated below, the molecules II and IV above the *xy*-plane. Copper-sulphur coordination indicated by broken lines.

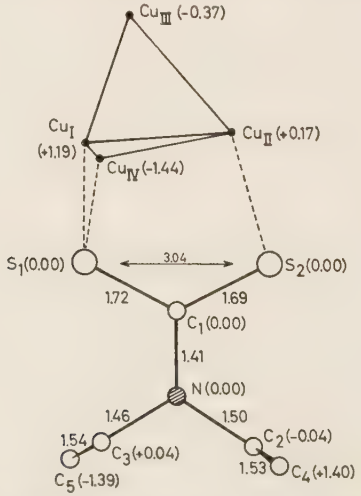

Fig. 4. Diethyldithiocarbamate molecule and copper tetrahedron. Orthogonal projection on the least squares plane corresponding to $S_1S_2C_1NC_2C_3$. The numbers in parentheses give the deviations (in Å) of the atoms from this plane. Other numbers correspond to interatomic distances (in Å). Copper-sulphur coordination indicated by broken lines.

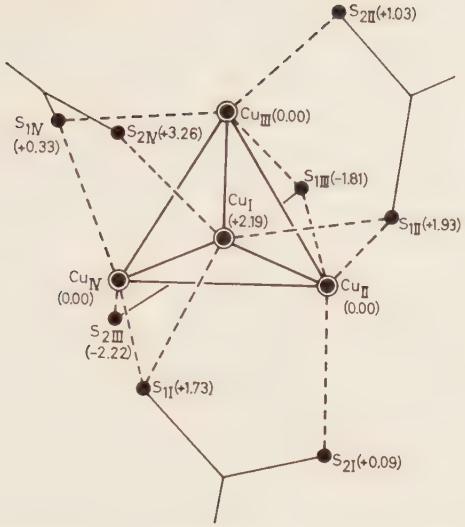

Fig. 5. Central part of a $[(C_2H_5)_2NCS_2Cu]_4$-molecule. Orthogonal projection on the $Cu_{II}Cu_{III}Cu_{IV}$-plane. The numbers in parentheses give the deviations (in Å) of the atoms from this plane. Copper--sulphur coordination indicated by broken lines.

The $[(C_2H_5)_2NCS_2Cu]_4$-molecule

This molecule, which has the symmetry $\bar{4}$, is illustrated in Fig. 3. It comprises a central Cu_4-tetrahedron surrounded by four diethyldithiocarbamate molecules. The tetrahedron is slightly distorted, with two copper-copper distances equal to 2.757 Å and four equal to 2.658 Å. In each case the calculated standard deviation is 0.005 Å. The last four of these Cu–Cu-distances are rather short and may be compared with those in the metallic phase of the element (2.56 Å).

Outside each of the faces of the central tetrahedron one diethyldithiocarbamate molecule is situated, by its sulphur atoms coordinating the copper atoms of the face. The linkage will be described in greater detail in a later section.

Diethyldithiocarbamate molecule

The $S_1S_2C_1NC_2C_3$-part of this molecule is practically coplanar. The normalized equation of the corresponding weighted least squares plane expressed in Ångström coordinates is:

$$-0.0327\,X+0.8147\,Y+0.5790\,Z-0.1136=0$$

The deviations of the atoms from this plane are:

S_1: -0.001 Å; S_2: 0.002 Å; C_1: -0.003 Å; N: 0.003 Å; C_2: -0.039 Å; C_3: 0.038 Å.

The diethyldithiocarbamate molecule projected on the least squares plane is seen in Fig. 4. The NC_2C_4- and NC_3C_5-planes are almost perpendicular to $S_1S_2C_1NC_2C_3$

(dihedral angles 89°3 and 88°9 respectively). The atoms C_4 and C_5 are situated on opposite sides of the $S_1S_2C_1NC_2C_3$-plane. Additional data for the molecule are given in Table 3.

Metal-ligand linkage

The linkage between metal atoms (A) and dithiocarbamate molecules (X) is schematically described in Fig. 6*c*. Each A is linked to three X and each X to three A.

The manner by which a dithiocarbamate molecule is attached to a face of the copper tetrahedron is seen in Fig. 4. One sulphur atom, S_1, coordinates two copper atoms, while the other, S_2, coordinates one. There are small variations in the sulphur-copper distances (average value 2.26(5) Å). The angle $C_1S_1Cu_I$ (112°9) differs significantly from the angles $C_1S_1Cu_{IV}$ (104°2) and $C_1S_2Cu_{II}$ (102°1).

The least squares plane of $S_1S_2C_1NC_2C_3$ passes close to one of the copper atoms (Cu_{II} in Fig. 4, distance 0.17 Å) and to the center of the tetrameric molecule (distance 0.11 Å). It is nearly perpendicular to the adjacent face of the copper tetrahedron, the interplanar angle being 84.3. The relative orientations of the ligands to the different faces of the central tetrahedron are seen in Fig. 3 and 5.

The best illustration of the copper-coordination is given in Fig. 5. Each copper is coordinated by three sulphur atoms, namely two atoms S_1 and one atom S_2. The SCuS-angles (110.0; 121.3; 127°6) show significant deviations from 120°. The distances (3.72 Å; 3.96 Å; 4.04 Å) between the coordinating sulphur atoms are about equal to or somewhat longer than van der Waal's contact distances. The coordination is nearly, but not quite, planar, the distance from the copper atom to the plane of the coordinating sulphur atoms being 0.14 Å. The copper atom is situated on the inside of this plane, i.e. on the same side as the center of the molecule. The plane is not parallel to the opposite face of the copper tetrahedron, the interplanar angle being 25°9.

It may finally be remarked that the sulphur atom S_2 is situated close to (distance 0.09 Å) one of the planes of copper atoms (e.g. S_{2I} and the $Cu_{II}Cu_{III}Cu_{IV}$-plane in Fig. 5).

Discussion

Linkage

The geometry of the $[(C_2H_5)_2NCS_2Cu]_4$-molecule is rather complicated. With the help of some reasonable postulates as to the copper-sulphur coordination, it can, however, be shown that the observed structure affords one of the simplest and most regular types of linkage producible by combining metal atoms and dithiocarbamate molecules in a 1:1 ratio. The postulates, which will be discussed later, are as follows:

1. Each copper atom should coordinate more than two sulphur atoms.
2. The sulphur atoms coordinated by a copper atom should be situated in different dithiocarbamate molecules.

Under these conditions each copper atom (A) should be linked to at least three dithiocarbamate molecules (X) and the composite $(AX)_p$-molecule should then be at least trimeric. Monomers are thus excluded as are also dimers. Under the same conditions each A in a trimer should be linked to three X and each X to three A. The sterical arrangements based on this type of linkage are, however, unreasonable

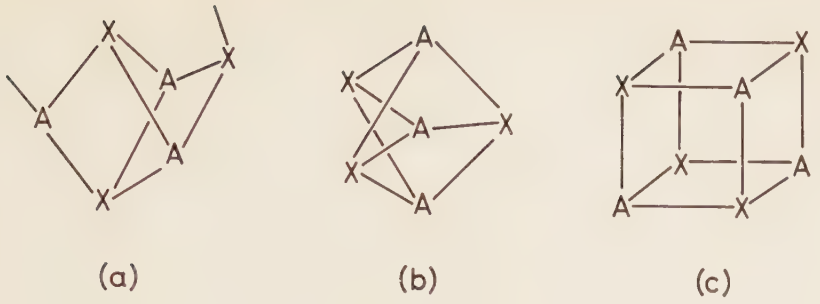

Fig. 6.

for the compound under consideration (Fig. 6*a*, *b*). Trimers are thus excluded and the simplest polymer must be at least tetrameric.

The different A — X link combinations compatible with the above postulates have been systematically derived for $(AX)_4$ polymers. (Some methods of representing and deriving such combinations will be given in a later paper.) Most of the sterical arrangements corresponding to these combinations are unreasonable for the compound under consideration, for instance all those in which any A is linked to more than three X. The most regular of the possible $(AX)_4$-arrangements is that given in Fig. 6*c*. It affords the only type of A — X-linkage in a tetramer in which each A is linked to three X and each X to three A. In this arrangement, which is that of copper(I)-diethyldithiocarbamate, there is an A_4-tetrahedron, with one X attached to each of its faces.

With the general linkage shown in Fig. 6*c*, each dithiocarbamate molecule should coordinate three copper atoms, namely those of the adjacent face of the tetrahedron. With both of the sulphur atoms of the molecule engaged in coordination one of them (denoted S_1) should coordinate two copper atoms and the other (denoted S_2) one, in accordance with the postulates. (The possibility that one of the sulphur atoms should not be engaged in coordination seems less likely and leads, moreover, to extremely short copper-copper distances or very pronounced irregularities in the SCuS or C_1SCu angles.) The above described manner in which a dithiocarbamate molecule should be attached to a tetrahedron face is shown schematically in Fig. 7*a* (cf Fig. 4) and still more simply in Fig. 7*b*, in which only the approximate position of S_1 is indicated.

Clearly three main orientations are possible for the molecule relative to the face (Fig. 7*b*, *c*, *d*), and when all four faces are considered a number of combinations can be obtained, corresponding to six essentially different types of linkage (enantiomorphs neglected). These are represented by Fig. 7 *e–j* where the central tetrahedron is seen projected on one of its faces. The manner in which the dithiocarbamate molecules are attached to the various faces is indicated by strokes as in Fig. 7*b–d*. (Fig. 7*e* corresponds exactly to Fig. 5.) Of these alternatives, those given in Fig. 7*e* and *f* are the most regular. However, the type of linkage represented by Fig. 7*f*, results in either extremely short Cu–Cu distances, strongly deformed copper coordinations or very pronounced irregularities in the C_1SCu-angles. In this type of arrangement pairs of CuS_3-coordination triangles share edges (Fig. 8*a*). Sharing of such triangle edges also occurs in structures represented by Fig. 7*h–j*.

The regular linkage represented by Fig. 7*e* is that of the observed structure (cf Fig. 5). In this instance the copper-sulphur coordination triangles share corners as

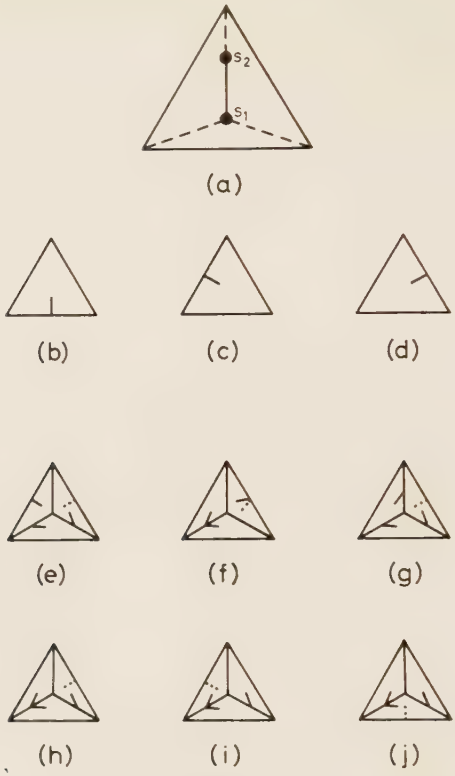

Fig. 7.

illustrated in Fig. 8*b*. The actual arrangement is obtained from that shown in the figure by folding the triangles alternatively upwards and downwards from the plane of the figure and then deforming and folding the central square so that the S_1-atoms

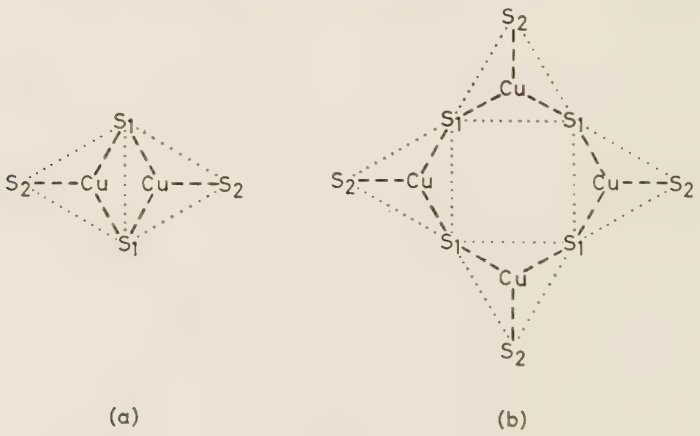

Fig. 8.

form a tetrahedron. In a model of this type with fixed regular threefold coordination and fixed S_1-S_2-distances (between sulphur atoms in the same dithiocarbamate molecule) and the symmetry $\bar{4}$, there would still be one degree of freedom. This arrangement will be discussed later in more detail.

In this way all conceivable arrangements, compatible with the postulates regarding the copper-sulphur coordination, have been systematically examined for possible lowest polymers of copper(I)diethyldithiocarbamate. It is found that there is no reasonable alternative which affords a simpler and more regular type of linkage than that realized in the observed structure. Fourfold copper coordination is not possible in any plausible low polymers, at least up to tetramers. Considering tetramers, an investigation of alternatives to the observed type of linkage shows that all correspond to arrangements with very short Cu–Cu distances and/or pronounced irregularities in the valency angles. None of the alternative types seems very plausible compared with that of the observed molecule, and it seems rather unlikely that any isomers to this could be isolated. The occurrence of a central Cu_4-tetrahedron in the observed molecule may be regarded as a result of the Cu–S linkage. The possibility of additional bond interactions will be considered later.

The above postulates will be considered in the next section. If in the discussion of possible types of linkage the postulates had been replaced by a simple statement that the copper atoms should coordinate sulphur atoms, a great number of arrangements with strongly distorted SCuS and C_1SCu angles or with twofold or single copper coordination would have been taken into account. Among these additional alternatives the following could be mentioned: a dimer with twofold copper coordination; a tetramer, very similar to the observed one but with very strongly deformed *fourfold* copper coordination and with distorted C_1SCu angles. (In the latter case the sulphur atom S_1 coordinates three copper atoms while S_2 coordinates one.)

It should be mentioned that the general type of $A-X$-linkage given in Fig. 6*c* is also found in some $(AXR_n)_4$-compounds, for instance $[(C_2H_5)_3AsCuI]_4$, [19], (A = Cu; X = I) or $[(CH_3)_3PtCl]_4$, [20], (A = Pt; X = Cl), in which metal tetrahedra also occur. Since the conditions in these compounds are different in many respects from those in $[(C_2H_5)_2NCS_2Cu]_4$, they cannot be discussed in quite the same way. Considering only the linkage, however, it can easily be shown that the structure of trimethylplatinum chloride, for instance, is of the simplest and most regular type compatible with sixfold coordination of platinum and single coordination of the CH_3-groups. The Pt–Pt distances are not particularly short in this compound.

Interesting linkage problems, similar to those encountered in the study of copper(I)-diethyldithiocarbamate, are probably to be expected when considering a number of other $(AX)_p$- and also $(AXR_n)_p$-compounds. Isomers may perhaps be obtained in some cases.

Copper coordination

Two-, three- and fourfold coordination of the metal atom has been found in compounds of monovalent copper. In most cases the highest possible number of metal-ligand bonds is formed. Fourfold coordination, corresponding to sp^3 bonding, is thus by far the most common type. Twofold coordination is represented only by a few compounds where its occurrence seems to be due to special conditions. (Even in AgCuS or Cu_9S_5, where the number of available valency electrons per copper atom is low, the copper coordination is reported to be higher than twofold, [31, 34].) In a number of complex sulphides, for instance wolfsbergite, $CuSbS_2$, [21], and stannite,

Cu_2FeSnS_4, [22], the copper atoms are tetrahedrally surrounded by sulphur atoms. Tetrahedral copper-sulphur coordination is also found in the organic complexes $Cu[SC(NH_2)_2]_3Cl$, [23], and $Cu[SC(NH_2)(CH_3)]_4Cl$, [24]. The postulate in the linkage discussion, that each metal atom in copper(I)diethyldithiocarbamate should coordinate more than two sulphur atoms, is thus very reasonable.

Twofold copper coordination is found in some oxides, e.g. Cu_2O, [25], $CuFeO_2$, [26], $CuCrO_2$, [27], and in diazoaminobenzene copper(I), DAB.Cu(I), [28]. In Cu_2O, when regarded as a covalent compound, there are on average four valency electrons available per copper atom or eight per oxygen atom. It is thus reasonable, that each copper should form two and each oxygen four bonds. The tendency of copper(I) to acquire fourfold coordination is obviously not strong enough for the formation of electron deficient bonds in this case. The other oxides could perhaps be considered in a similar way. In the case of DAB. Cu(I), the twofold copper coordination found in the dimeric molecule, $[(C_6H_5-N=N-N-C_6H_5)Cu]_2$, is apparently due to the coordinating properties of the ligands. Owing to the bond conditions in the organic molecules, planar trigonal bonding seems to be more likely than tetrahedral for the nitrogen atoms. Each nitrogen would accordingly not coordinate more than one copper atom. Moreover, for topological and sterical reasons it appears unlikely, that more than two nitrogen atoms per molecule would be engaged in such bonds. There would consequently be only two nitrogens available for each copper atom to coordinate. An arrangement of the copper(I)diethyldithiocarbamate type would be impossible under these conditions. (In the dimer of DAB. Cu(I) the metal atoms are probably also engaged in delocalized interactions, which may contribute to the stabilization of the molecule. In fact on a basis of sterical considerations alone it is very difficult to find any plausible alternative to the dimer under discussion.)

Threefold copper coordination has been reported to occur in $KCu(CN)_2$, [29], $KCu_2(CN)_3H_2O$, [30], and in some complicated sulphide structures, e.g. in stromeyerite AgCuS, [31], covelline, CuS, [32], [33], and Cu_9S_5 (low temperature form), [34]. Clearly the atomic arrangements in these compounds are determined by a number of different factors interacting in a very complicated way and no attempts will be made here to analyze them. The numbers of available valency electrons together with topologic and steric factors and delocalized electronic interactions are probably of importance, and possibly also the entropy conditions and kinetics associated with the formation of the compounds. The occurrence of delocalized interactions in the sulphides seems to be indicated by the fairly metallic properties of these compounds.

As is to be expected the mean copper-sulphur distance, 2.26(5) Å, in copper(I)-diethyldithiocarbamate is shorter than those for tetrahedral coordination in $Cu[SC(NH_2)_2]_3Cl$ (2.37 Å, average) and $Cu[SC(NH_2)(CH_3)]_4Cl$ (2.34 Å, average). It may be compared with the Cu–S-distances for threefold coordination in AgCuS (2.28 Å, average) and Cu_9S_5 (2.26 Å). The corresponding distance in CuS (2.19 Å) is appreciably shorter. The accuracy of the last three distance values, however, does not seem to be very high.

The copper-sulphur coordination in copper(I)diethyldithiocarbamate is not quite regular and planar but the deviations from 120° in the S–Cu–S angles are not greater than 10°. If a copper atom were to coordinate two sulphur atoms (at distances of 2.27 Å) in the same dithiocarbamate molecule (with $S_1S_2 = 3.04$ Å), then the S–Cu–S angle would be about 84°, i.e. 36° less than 120°. With fourfold coordination the Cu–S-distance would be longer and an angle of about 80° would be obtained. This is nearly 30° less than the tetrahedral angle. Moreover, the C_1SCu angles would be strongly

distorted, giving values of about 75°. It is thus very reasonable that such an unfavourable configuration should be avoided whenever possible. Arrangements where it would occur are accordingly neglected in the linkage discussion (second postulate).

The deviations from regular coordination, found in the observed structure, and their possible connection with additional stabilization of the molecule by delocalized interactions will be discussed in a later section.

Dithiocarbamate molecule

The interatomic distances in the diethyldithiocarbamate molecule are perhaps not accurate enough to permit of conclusions regarding bond orders. Some important features of the molecular geometry should, however, be taken into consideration. The $S_1S_2C_1NC_2C_3$ part is practically planar, which indicates double bond character for the C_1-N bond. Thus there would be an electron displacement in the molecule towards the sulphur atoms. This is in accordance with infrared studies by Chatt *et al.* [35] and with some other structure determinations of dithiocarbamates, e.g. $[(C_2H_5)_2NCS_2]_2Ni$, [36], $[(CH_3)_2NCS_2]_2Co(NO)$, [37], $[(n\text{-}C_3H_7)_2NCS_2]_2Cu$, [38].

The carbon atoms C_4 and C_5 are situated on opposite sides of the $S_1S_2C_1NC_2C_3$ plane and are thus in trans position relative to it. Owing to the presence of the hydrogen atoms and to the molecular geometry the energetically favourable regions of possible C_4 and C_5 positions seem to be fairly restricted, even if the environment of the molecule is not taken into consideration. This may be of importance for the space filling properties of the molecule. Limited regions corresponding to cis position may also be favourable. In fact cis configuration has been found in a silver(I)diethyldithiocarbamate structure (to be published).

Additional interactions

The SCuS-angles in the crystal structure are 110°0, 121°3 and 127°6. The distance from the copper atom to the plane of the coordinating sulphur atoms is 0.14 Å. Thus there are noticeable deviations from a strictly regular and planar configuration in the copper coordination. Such a planar and regular configuration, however, is geometrically quite possible in a model involving only copper and sulphur atoms. A model of this kind with the symmetry $\bar{4}$ and with Cu–S = 2.27 Å and $S_1S_2 = 3.04$ Å (in the same dithiocarbamate molecule) has been studied. This model has one degree of freedom, when its position and orientation in space are not taken into account. Calculations were performed with the z-coordinate of an S_1-atom, z_{S_1}, as the independent variable (z-axis along $\bar{4}$, origin at the inversion centre). Plausible arrangements were found for $1.0 \leq z_{S_1} \leq 1.4$ (z_{S_1} in Å). In this z_{S_1}-interval the Cu_I–Cu_{II} and Cu_I–Cu_{III} distances (cf. Fig. 3) were never below 2.75 and 2.98 Å respectively. The short copper-copper distances (Cu_I–Cu_{II} 2.66 Å, Cu_I–$Cu_{III} = 2.76$ Å) in the crystal structure are obviously not a necessary consequence of the Cu–S-linkage as far as only copper and sulphur atoms are considered.

If in the regarded model the C_1-atoms are introduced such that the C_1S_1Cu angles are equal and C_1–$S_1 = C_1$–$S_2 = 1.70$ Å, then $\angle C_1S_1Cu$ varies from 110° to 122° and $\angle C_1S_2Cu$ from 97° to 87° in the z_{S_1}-interval considered. The angle values 110° and 97°, which are closest to those in the crystal structure ($\angle C_1S_1Cu = 112°9$ and 104°2; $\angle C_1S_2Cu = 102°1$), are obtained for $z_{S_1} = 1.0$. It may be added that for $z_{S_1} < 1.0$,

unfavourably short sulphur-sulphur distances occur in the model. For $z_{S_1} > 1.4$ the C_1S_2Cu angle is still more distorted than it is in the interval considered.

Applying the above assumptions about distances and angles it is evidently not possible to construct a plausible model with *planar and regular* copper coordination, if the C_1SCu angles are to have values within the range of the corresponding observed angles (102–113°). It is, however, possible to obtain such angle values, if the copper atoms in the model, for $z_{S_1} = 1.0$, are moved *outwards* from the respective planes of the coordinating sulphur atoms. In the crystal structure, however, the copper atoms are situated on the "*inside*" of these planes. It is accordingly not likely that the short Cu–Cu distances are caused by requirements of the C_1SCu angles. (The C_1SCu angles may, however, geometrically influence various details of the structure, i.e. in order to avoid strong distortions in these angles, changes from "expected" values may be necessary among other geometrical elements. Such geometrical dependences will be discussed in the next section.)

According to the above study the short metal-metal distances observed do not appear to be a consequence of requirements of other geometrical elements (distances, angles) considered so far. Thus it is reasonable to expect that the copper atoms, in addition to their engagement in local Cu–S bonds, also take part in some other interactions by which they are forced together. Delocalized bonding interactions, involving the metal atoms and the inner parts of the dithiocarbamate molecules, may then be considered. The approximate $CuS_1S_2C_1NC_2C_3$ coplanarity may be an indication of such interactions. (In the above model with planar and regular copper coordination the distance from the copper atom coordinated by S_2 to the $S_1S_2C_1$ plane is 1.2 Å for $z_{S_1} = 1.0$.) It may be noticed that a similar metal-ligand coplanarity also occurs in $Cu[SC(NH_2)(CH_3)]_4Cl$, [24]. It may also be mentioned that the S_2 atoms in the crystal structure are situated close to planes of copper atoms. Direct Cu–Cu bonding could also be considered. In order to get a clear view of the nature of these possible interactions, the information from the structure determination has to be completed by other investigations. The additional interactions probably contribute to the stabilization of the molecule.

Short Cu–Cu distances have been found in some other organic copper complexes, for instance DAB.Cu(I) (2.45 Å, Cu_2-pair), [28], $[(C_2H_5)_3AsCuI]_4$ (2.60 Å, regular Cu_4-tetrahedron), [19], $[CuAc_2H_2O]_2$ (2.64 Å, Cu_2-pair), [39] and some compounds related to the latter. They may be compared with the distance of 2.56 Å between adjacent atoms in metallic copper. The short Cu–Cu distances, at least in DAB.Cu(I) and $[CuAc_2H_2O]_2$, may very well be due to the geometry of the molecules. Appreciably longer distances would thus give rise to strongly deformed copper coordination. This does not, however, exclude the possibility of bonding interactions between the metal atoms. Thus, according to Figgis and Martin, [40], magnetic data from $[CuAc_2H_2O]_2$ indicate the existence of very weak covalent Cu–Cu bonds in this compound.

Short metal-metal distances have also been found in some investigated dithiocarbamates of silver and gold (to be published).

Geometrical dependences

The geometrical dependences among the SCuS and C_1SCu angles should be briefly considered. In a model of a tetramer composed of the atoms Cu, S_1, S_2 and C_1 with the symmetry $\bar{4}$ and the linkage described earlier, the degrees of freedom are 5, if the

Cu–S bond distances and the C_1 S and S_1S_2 distances in the same dithiocarbamate molecule are fixed and the position and orientation of the model are neglected. No assumptions are then made as to the angles. The number of SCuS and C_1SCu angles considered is 6 and thus exceeds that of the degrees of freedom by one unit. Accordingly geometrical dependences must occur among these angles. With the C_1S_1Cu angles postulated to be equal there would be 4 degrees of freedom and 5 angles to consider and so on. If no assumption is made about the symmetry, the degrees of freedom are 18 but the number of angles considered is 24, and dependences still occur. If coplanarities are postulated between the copper atoms and the corresponding $S_1S_2C_1$ planes, the number of degrees of freedom is further reduced. Other elements of the structure, for instance Cu Cu distances and intermolecular contacts, may also be of interest when the geometrical dependences are considered.

The significant difference between the C_1S_1Cu angles might be ascribed to the $CuS_1S_2C_1NC_2C_3$ coplanarity or to the packing of the molecules, but is probably caused by several factors.

The geometrical considerations above may serve to illustrate the difficulties in drawing definite conclusions from the finer details of a complicated crystal structure like copper(I)diethyldithiocarbamate. The angles and distances are influenced by many factors and the purely geometrical dependences are certainly of great importance.

A relation for the calculation of the degrees of freedom in a model is given in the Appendix.

Some final remarks

A great number of AX-compounds, in which A is a metal and X some ligand atom or molecule, are built up as high polymers in the solid state. CsCl, AgCl, ZnS, $BaSO_4$ may be mentioned as examples. In such polymers it is often possible to realize fairly high coordination numbers for A and X. It is accordingly interesting to consider the reason why copper(I)diethyldithiocarbamate forms low polymer molecules instead of some type of high polymer, in which copper perhaps could have attained its normal fourfold coordination. It is not intended to give a definite answer to this question here. However, a few factors, some or all of which may be of importance, should be mentioned briefly.

The *bond conditions* in the tetramer may be particularly convenient for its stabilization. The possibility of delocalized bonding, perhaps including Cu Cu interactions, has already been discussed.

Thermodynamic and *kinetic* effects may be of considerable importance. The compound is formed in the presence of a solvent and the entropy gain is in favour of the formation of soluble low polymers, which may also be the most easily obtainable for kinetic reasons. Once they are formed, their active central parts (containing Cu and S) are fairly well *shielded* by the inert organic groups. Subsequently, on crystallization the solid phase may, again for kinetic reasons, be most easily built up from the tetramers present in the solution. The occurrence of tetramers in solution has been proved by Åkerström [2].

For *sterical* reasons a high polymer of copper(I)diethyldithiocarbamate in which copper has fourfold (tetrahedral) coordination may be unfavourable. Thus in AX-compounds, where X is a bulky group, which can only coordinate in a very unsymmetric way, the packing conditions can often make high coordination impossible. The situation is illustrated by a two-dimensional (purely hypothetical) example in Fig. 9.

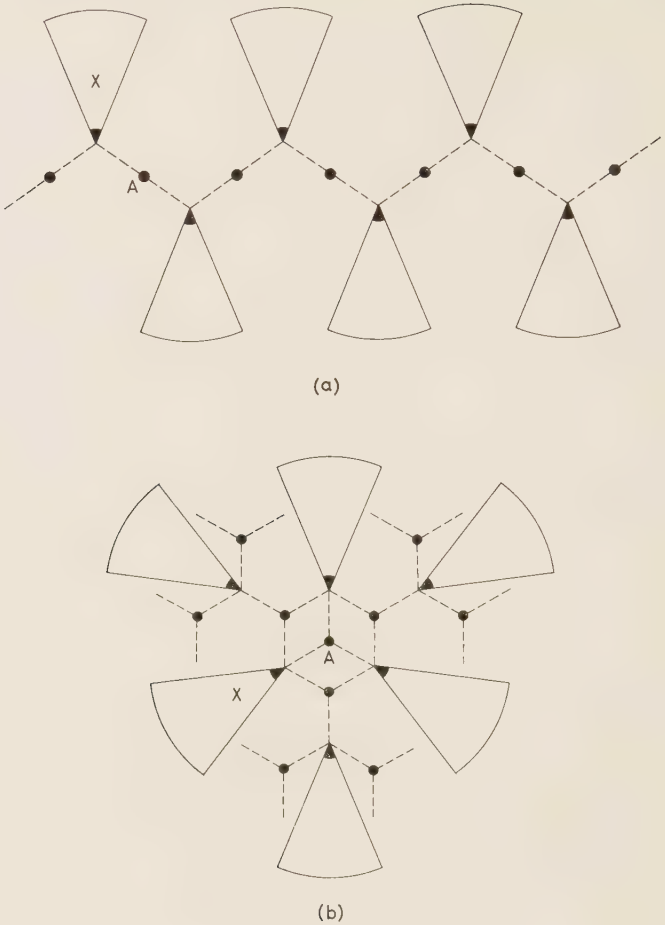

Fig. 9.

In this instance twofold coordination is possible (Fig. 9*a*), but it is evident that *AX*-arrangements which give threefold coordination to each *A* and *X*, cannot be constructed in the example given. Thus, starting the construction from a given *A* (Fig. 9*b*), its nearest and next nearest *X*-neighbours can be accommodated, but then some, at least, of the second next nearest *X*-neighbours must overlap other *X*-objects. The overlapping would be still more pronounced in the event of higher coordination.

Similar difficulties in attaining high coordination numbers can arise in three-dimensional arrangements of the considered type of compounds. The *X*-molecules coordinating a certain *A*-atom may be termed "first order neighbours" to this atom. The other *A*-atoms which are coordinated by the first order neighbours may be called "second order neighbours" to the first mentioned *A*-atom. The *X*-molecules, with the exception of first order neighbours, coordinating the second order neighbours may be called "third order neighbours", and so on. The $(n\ 1)'$th order neighbours are accordingly coordinated only by the $(n\ 2)'$th and n'th order neighbours. When a

proposed type of linkage is impossible because there is not space for a sufficient number of first order neighbours around an A, the situation might be described as one of "first order steric hindrance". When it is possible to accommodate the first order neighbours but not the second order neighbours the situation might be described as one of "second order steric hindrance". The concept "n'th order steric hindrance" is defined correspondingly. For $n > 1$ it can be convenient to use the term "higher order steric hindrance". The possibility of not only first but also higher order steric hindrance has to be taken into account when discussing coordination polymers.

It may be mentioned that while the higher homologues of the dialkyldithiocarbamates of copper(I) occur as soluble low polymers, the dimethyl compound is insoluble in all common organic solvents [2], which may indicate that it is a high polymer. In this compound the space requirements and the shielding properties of the organic groups are less pronounced than in the higher homologues.

APPENDIX

Degrees of freedom and geometrical dependences in model arrangements

A general view of the geometrical dependences in a complicated chemical arrangement may in many cases be obtained from a study of the degrees of freedom of a model with certain properties postulated. The model may correspond to a complete crystal structure or to an isolated group of atoms. The atoms (regarded as at rest—average positions considered) are represented by points in the model. The position and orientation of the model in space will be neglected when considering the degrees of freedom.

Postulates regarding the model are made in the following order:

1°. The symmetry (space group or point symmetry) is given. All information about the symmetry should be obtainable from 1°.
2°. The distribution of points (atoms) on general and special positions is given. It is only necessary to consider points which are unrelated by symmetry (non-equivalent points) when giving this description.
3°. Some *additional postulates*, relating the points to each other, are made. The additional postulates concern linearities, planarities, distances, angles and equalities between distances or angles.

The postulates should be formulated in such a way that the following conditions are fulfilled:

a) The model should be constructable, i.e. the postulates should not contradict each other.
b) No postulated property of the model under consideration should be obtainable from other postulated properties. The properties given by 3° should accordingly be independent of each other and should not be obtainable from 1° and 2°.

The degrees of freedom are given by the following formula:

$$F = S + D - A$$

Three-dimensional structures are considered below, but the relation can also be

Table 4. S-values for some point symmetries in finite arrangements.

Point symmetry		S
1		-6
$\bar{1}$; m		-3
X	$(X \geqslant 2)$	-2
$\bar{X}$	$(X \geqslant 3)$	-1
X/m ; Xm	$(X \geqslant 2)$	-1
$X2$; X/mm	$(X \geqslant 2)$	0
$\bar{X}2$; $\bar{X}m$	$(X \geqslant 3)$	0
Cubic point symmetries		0

X is the symbol of an X-fold rotation symmetry axis.
$\bar{X}$ is the symbol of an X-fold inversion axis.
Besides the restrictions in the table above X can have any positive integral value, e.g. 5, 7, 11.

applied to two- and one-dimensional arrangements. It is convenient to present the magnitudes in the formula in the order: F, D, S, A.

F is the number of degrees of freedom of the model under consideration, if its position and orientation in space are neglected. $F \geqslant 0$. $F = 0$ for a rigid model.

D is determined by the point distribution, postulate 2°, and is given by the expression:

$$D = \sum_i n_i f_i$$

n_i is the number of non-equivalent points, each of which has f_i degrees of freedom when only the postulates 1° and 2° are considered. $0 \leqslant f_i \leqslant 3$. f_i is equal to 3 for a general position but has lower values for special positions. For instance $f_i = 2$ for a point situated on a mirror plane only, 1 for a point on a rotation symmetry axis only, 0 for a point at an inversion centre, and so on.

S is a symmetry constant which is determined by postulate 1°. It accounts for the requirement that the position and orientation of the model in space should be neglected, i.e. that only relative positions within the model are considered. It also accounts for the degrees of freedom of the unit cell dimensions and angles in crystal structures.

For a finite model, corresponding to a given isolated set of atoms, $-6 \leqslant S \leqslant 0$. S is determined by the point symmetry of the arrangement. Thus $S = -6$ in general non-symmetric cases. $S = -3$ if the only symmetry element is a centre of symmetry or a mirror plane, -2 for a single n-fold ($n > 1$) rotation symmetry axis, -1 for a single three-, four- or sixfold inversion axis, and so on. S-values corresponding to different point symmetries of finite models are given in Table 4.

For a model of a complete crystal structure, $+1 \leqslant S \leqslant +6$. S is determined by the point group symmetry. It has accordingly the same value for all the space groups belonging to a given point group. S-values corresponding to different symmetries of crystal structures are listed in Table 5.

A is the reduction in the number of degrees of freedom due to the *additional postulates* (3°). $A \geqslant 0$. $A = 0$ when no postulate is given in 3°.
The postulates in 3° may be expressed by equations involving the point coordinates. In general A is equal to the number of these equations if they are given in the following way:

Table 5. S-values for different symmetries in crystal structures.

Crystal system	Point group	Space group No.[a]	S
Triclinic	1	1	3
	$\bar{1}$	2	6
Monoclinic	m	6–9	2
	2	3–5	3
	$2/m$	10–15	4
Orthorhombic	$mm2$	25–46	2
	222; mmm	16–24; 47–74	3
Tetragonal	4; $4mm$	75–80; 99–110	1
	$\bar{4}$; $4/m$; 422; $\bar{4}2m$; $4/mmm$	81–98; 111–142	2
Trigonal	3; $3m$	143–146; 156–161	1
	$\bar{3}$; 32; $\bar{3}m$	147–155; 162–167	2
Hexagonal	6; $6mm$	168–173; 183–186	1
	$\bar{6}$; $6/m$; 622; $\bar{6}m2$; $6/mmm$	174–182; 187–194	2
Cubic	All cubic point groups	195–230	1

[a] According to International Tables for X-ray Crystallography, I, 1952.

One equation for each postulated distance or angle. One equation for each postulated equality between two distances or two angles. One equation for a postulated planarity between four points. In general a postulated linearity between three points should be expressed by two equations, not obtainable from each other. In certain cases, however, this is not possible and one equation is given. Such cases may occur when one or more points in special positions are involved in the linearity. For instance: a linearity between the points $(0,0,z_1)$, (x_2,y_2,z_2) and $(\bar{x}_2,\bar{y}_2,\bar{z}_2)$ is expressed by the equation: $z_1=z_2$. Linearities obtainable from the symmetry and point distribution are not postulated in 3^c and will accordingly not give any contribution to A.

It is usually not necessary to formulate the equations in order to obtain A.

In certain borderline cases the value of A can differ from the number of equations as given above. Such cases may for instance occur if linearities are expressed by postulates concerning distances or angles.[1] Borderline cases are usually of little interest when considering models of chemical arrangements.

The additional postulates $(3')$ may correspond to descriptions of complete molecules of known geometry, or only to certain bond distances and angles or other geometrical properties which in the discussion are regarded as fixed. Interatomic contacts may be considered, for example.

[1] A more general borderline case is given below:

Consider a model. Replace one of the postulated values (distance or angle) by any new fixed value, differing from the foregoing by a small amount, while all other postulated properties remain unchanged. If then the proposed resulting model is not constructable, or if its number of degrees of freedom deviates from that of the original model, however small the difference between the two values of the distance or angle under consideration may be, then the original model represents a borderline case.

Dependences

In a given model with F degrees of freedom, consider an arbitrarily chosen set of geometrical elements (distances, angles), the values of which are not postulated. Let C be the number of these elements. Then if $C > F$, there are *geometrical dependences* among the considered elements, i.e. the values of some or all of the distances and angles under consideration are interdependent and/or depend on the postulated properties of the model.

In many chemical arrangements the distances and angles can influence each other through geometrical dependences. In this way the deviations from "normal" values may be appreciable. The CCC-angles in cyclopropane may be mentioned as extreme examples. In crystal structures the geometrical dependences are often very complicated. In such cases it can be difficult to draw conclusions from values of bond distances and angles, even if the structure is very accurately determined. If any distance or angle in a structure is discussed in a quantitative manner, it is advisable also to consider all other distances and angles of chemical or physical interest and to investigate the possible geometrical dependences among the elements under consideration. The interatomic "contacts" can be of interest in this connection.

Rigid polypoint objects

When polypoint objects (representing molecules or other structural fragments), which are postulated to be *rigid*, occur in the model it may be convenient to put the f_i-values of these objects directly into the expression: $D = \sum_i n_i f_i$. A corresponding simplification in A is then also made.

In this instance the postulates regarding the model are made in the following order:

1°. Complete descriptions of the individual polypoint objects are given. 1° should not give any information about the relative positions and orientations of the objects.
2°. The symmetry of the model is given.
3°. The distribution of single points and polypoint objects on general and special positions is given.
4°. Additional postulates are made, relating the single points and polypoint objects to each other. Besides the properties considered in the earlier treatment point coincidences can also be included here. Point coincidences should be expressed by coordinate equality postulates.

The postulates should be formulated in such a way that the following conditions are fulfilled:

a) The model should be constructable.
b) In the model under consideration no postulated property given by 4° should be obtainable from other postulated properties (given by 1°–4°).

$D = \sum_i n_i f_i$ is determined by postulate 3°. f_i is the number of degrees of freedom of an individual object, when only the postulates 1°, 2° and 3° are considered. The position and orientation of the object are then taken into account. $f_i = 6$ for a non-linear rigid polypoint object in a general position. In special positions f_i has other

easily obtainable values. n_i is the number of non-equivalent objects each of which has f_i degrees of freedom.

S is determined by the symmetry of the model as in the earlier treatment.

A is the reduction in the number of degrees of freedom due to the additional postulates, 4°. A is determined by the number of independent equations, expressing the additional properties, in the same way as in the earlier treatment. Considering point coincidences, there is one equation for each postulated coordinate equality. A single point coincidence between two polypoint objects usually contributes 3 units to A. However, if two rigid polypoint objects have two points in common, the contribution is usually 5. This may for instance be applied to rigid polyhedra with common corners or common edges.

SUMMARY

The crystal structure of copper(I)diethyldithiocarbamate has been determined from single crystal X-ray data. The crystals are tetragonal, space group $P\bar{4}2_1c$, $a = 13.49$ Å, $c = 9.33$ Å.

The copper positions were obtained from the three-dimensional Patterson function and the sulphur positions from electron density projections. The nitrogen and carbon positions were determined from a difference synthesis projection, interpreted by geometrical constructions. The structure was refined by three-dimensional least squares analysis ($R = 0.11$).

The structure comprises discrete tetrameric molecules (symmetry $\bar{4}$), of which there are two per elementary cell. The $[(C_2H_5)_2NCS_2Cu]_4$ molecule contains a slightly distorted Cu_4-tetrahedron with short metal-metal distances (2.66 and 2.76 Å). The diethyldithiocarbamate molecules are situated outside the faces of this tetrahedron and coordinate the metal atoms by copper-sulphur bonds. The copper coordination is *threefold* but not quite planar, the metal atoms being situated 0.14 Å "inside" the plane of the coordinating sulphur atoms. Some of the SCuS-angles show significant deviations from 120° but the variations in the Cu–S distances (average value 2.27 Å) are small. The sulphur atoms and their four closest neighbours (C_1, N, C_2, C_3) in the diethyldithiocarbamate molecule form an almost planar arrangement, indicating double bond character for the C_1–N bond. One of the copper atoms coordinating the dithiocarbamate molecule is situated close to the $S_1S_2C_1NC_2C_3$-plane.

In the discussion, attempts are made to analyze the main factors which may be responsible for the observed structure, and a number of problems of far reaching interest are encountered. Special emphasis is given to the geometrical and topological aspects. A systematic study of alternative arrangements demonstrates that although the $[(C_2H_5)_2NCS_2Cu]_4$-molecule has a complicated structure it nevertheless affords one of the simplest and most regular types of possible linkage between the metal atoms and dithiocarbamate molecules. In low polymers up to tetramers no alternative type of linkage seems very plausible compared with that of the observed molecule. Tetrahedral copper-sulphur coordination, unless strongly deformed, is not possible in low polymers, at least up to tetramers. The occurrence of a central Cu_4-tetrahedron may be regarded as a result of the copper-sulphur linkage. However, the situation does not seem to be completely explainable only by the topology of local metal-ligand bonds. Thus, from a geometrical study it is found that the short metal-metal distances observed are not necessarily caused by such bond interactions. It is accordingly probable that the copper atoms are also engaged in delocalized bonding, perhaps including Cu–Cu interactions.

There are significant variations in the values of certain bond angles in the structure. An examination of these angles shows, however, that they are not geometrically independent. It is accordingly difficult to draw conclusions from an isolated study of them. Conversely, certain demands in these angles might influence other details of the structure. It is of course important

to keep such purely geometrical dependences in mind when discussing a structure. A general view of such dependences may be obtained from studies of the degrees of freedom in idealized models. A relation for the calculation of the degrees of freedom in such models is given in the Appendix.

Finally, the question why the compound occurs as a low polymer and not as a high polymer is discussed. Among the factors that may be of importance, the bond conditions, thermodynamic and kinetic effects, and screening properties of the ligands are mentioned. The steric aspects of this problem are also considered and a concept termed "higher order steric hindrance" is introduced.

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to the head of this Institute, Professor Gunnar Hägg, who introduced me to the field of X-ray crystallography, for his encouragement and great interest in my work and for all the facilities he has placed at my disposal.

I am greatly indebted to Professor A. Fredga and Dr. S. Åkerström for supply of samples and for continuous information about their investigations on dithiocarbamates.

Further, I wish to express my sincere appreciation to Professor A. Magnéli and his coworkers for stimulating discussions and generous support.

For valuable discussions thanks are also due to Professor I. Lindqvist, Dr. T. Alfredsson, Dr. G. Bergson, Dr. I. Fischer-Hjalmars, Dr. S. Flodmark, and to my colleagues in the Department of Inorganic Chemistry.

The conscientious and skilful assistance of Mrs. H. Billander with the experimental and computational work is greatly appreciated. For very valuable help thanks are also due to Mrs. M. Englund and all other members of the secretarial and technical staff of this Institute.

This work has been financially supported by grants from the *Swedish Natural Science Research Council* which are gratefully acknowledged.

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REFERENCES

1. FREDGA, A., Rec. trav. chim. *69*, 416 (1950).
2. ÅKERSTRÖM, S., Arkiv Kemi *14*, 387 (1959).
3. HESSE, R., Acta Cryst. *13*, 1025 (1960).
4. HESSE, R., Advances in the Chemistry of the Coordination Compounds, p. 314, New York, 1961.
5. PARRISH, W., Acta Cryst. *13*, 838 (1960).
6. LONSDALE, K., Acta Cryst. *3*, 400 (1950).
7. HÄGG, G., and LAURENT, T., J. Sci. Instruments *23*, 155 (1946).
8. WESTMAN, S., BLOMQVIST, G., and ÅSBRINK, S., Arkiv Kemi *14*, 535 (1959).
9. ÅSBRINK, S., BLOMQVIST, G., and WESTMAN, S., Arkiv Kemi *14*, 545 (1959).
10. LIMINGA, R., and OLOVSSON, I., to be published.
11. ÅSBRINK, S., and BRÄNDÉN, C.-I., to be published.
12. CRUICKSHANK, D. W. J., The Equations of Structure Refinement, Abstracts from Manchester Summer School, 1960.
13. THOMAS, L. H., and UMEDA, K., J. Chem. Phys. *26*, 293 (1957).
14. TOMIIE, Y., and STAM, C. H., Acta Cryst. *11*, 126 (1958).
15. BERGHUIS, J., *et al.*, Acta Cryst. *8*, 478 (1955).
16. DAUBEN, C. H., and TEMPLETON, D. H., Acta Cryst. *8*, 841 (1955).
17. CRUICKSHANK, D. W. J., Acta Cryst. *2*, 65 (1949).
18. CRUICKSHANK, D. W. J., Acta Cryst. *3*, 72 (1950).
19. WELLS, A. F., Z. Krist. *94*, 447 (1936).
20. RUNDLE, R. E., and STURDIVANT, J. H., J. Am. Chem. Soc. *69*, 1561 (1947).
21. HOFMANN, W., Z. Krist. *84*, 177 (1933).
22. BROCKWAY, L. O., Z. Krist. *89*, 434 (1934).

23. KNOBLER, C. B., OKAYA, Y., and PEPINSKY, R., Z. Krist. *111*, 385 (1959).
24. TRUTER, M. R., and RUTHERFORD, K. W., J. Chem. Soc. *1962*, 1748.
25. STRUKTURBERICHT, I., p. 153, 222, Leipzig, 1931.
26. SOLLER, W., and THOMPSON, A. J., Bull. Am. Phys. Soc. *10*, 17 (1935).
27. DANNHAUSER, W., and VAUGHAN, P. A., J. Am. Chem. Soc. *77*, 896 (1955).
28. BROWN, I. D., and DUNITZ, J. D., Acta Cryst. *14*, 480 (1961).
29. CROMER, D. T., J. Phys. Chem. *61*, 1388 (1957).
30. CROMER, D. T., and LARSON, A. C., Acta Cryst. *15*, 397 (1962).
31. FRUEH, A. J., Z. Krist. *106*, 299 (1955).
32. OFTEDAL, I., Z. Krist. *83*, 9 (1932).
33. BERRY, L. G., Am. Mineral. *39*, 504 (1954).
34. DONNAY, G., *et al.*, Am. Mineral. *43*, 228 (1958).
35. CHATT, J., *et al.*, Suomen Kemistilehti *29*, 75 (1956).
36. SHUGAM, E. A., and LEVINA, V. M., Kristallografiya *5*, 257 (1960).
37. ALDERMAN, P. R. H., OWSTON, P. G., and ROWE, J. M., J. Chem. Soc. *1962*, 668.
38. PIGNEDOLI, A., and PEYRONEL, G., Gazz. Chim. Ital. *92*, 745 (1962).
39. VAN NIEKERK, J. N., and SCHOENING, F. R. L., Acta Cryst. *6*, 227 (1953).
40. FIGGIS, B. N., and MARTIN, R. L., J. Chem. Soc. *1956*, 3837.

Tryckt den 12 mars 1963

Uppsala 1963. Almqvist & Wiksells Boktryckeri AB